

L Number	Hits	Search Text	DB	Time stamp
1	0	("covalentwithadhesive").PN.	USPAT; US-PGPUB; EPO; JPO; DERWENT	2003/12/04 11:05
2	487	covalent with adhesive	USPAT; US-PGPUB; EPO; JPO; DERWENT	2003/12/04 11:31
3	12	(covalent with adhesive) and 623/\$.ccls.	USPAT; US-PGPUB; EPO; JPO; DERWENT	2003/12/04 11:32

	Document ID	KSc	Issue-De	Page	Tit
1	US 3556305 A	U	19710119	6	COMPOST
2	DE 2357121 A	D	19740530		Aminimi
3	DE 2461023 A	D	19750710		Prepoly
4	US 3895166 A	U	19750715	5	Bonded
5	US 3897585 A	U	19750729	5	Integra
6	US 3931084 A	U	19760106	10	Fluoroc
7	US 3979538 A	U	19760907	4	Flockec
8	US 3997349 A	U	19761214	8	Light-s
9	US 4003312 A	U	19770118	6	Prepari
10	US 4060081 A	U	19771129	16	Multila
11	GB 1518371 A	D	19780719		Laminat
12	US 4180442 A	U	19791225	10	Electro
13	US 4243771 A	U	19810106	4	Nitrile
14	JP 57058617 A	J	19820408		MEDICAL
15	US 4337111 A	U	19820629	4	Method
16	US 4337111 A	D	19820629		Introdu
17	US 4355078 A	U	19821019	3	Nitrile
18	US 4405427 A	U	19830920	11	Electro
19	JP 58185515 A	J	19831029		TAPE DE
20	JP 58185515 A	D	19831029		Tape-fo
21	US 4442142 A	U	19840410	3	Nitrile
22	JP 59098183 A	D	19840606		Joining
23	US 4460759 A	U	19840717	7	Adhesiv
24	US 4460525 A	U	19840717	10	Method
25	JP 60068083 A	J	19850418		FORMATI
26	US 4518449 A	U	19850521	6	Process
27	US 4522907 A	U	19850611	14	Method
28	US 4529772 A	U	19850716	7	Contact
29	US 4533307 A	U	19850806	9	Apparat
30	US 4536425 A	U	19850820	5	Method
31	US 4554301 A	U	19851119	9	Modifie
32	US 4554195 A	U	19851119	6	Ceramic
33	US 4572828 A	U	19860225	4	Method
34	US 4588838 A	U	19860513	9	Diurea
35	US 4588838 A	D	19860513		Addn. p
36	US 4618688 A	U	19861021	5	Silane
37	US 4619867 A	U	19861028		Azlacto
38	US 4626310 A	U	19861202		Surfact
39	EP 205145 A	D	19861217		Reactiv
40	US 4644032 A	D	19870217		Non-ghc
41	US 4645846 A	U	19870224		Silane
42	US 4671740 A	U	19870609		Ceramic
43	US 4677695 A	U	19870707		Web wit
44	US 4692557 A	U	19870908		Encapsu
45	US 4699843 A	U	19871013		Azlacto
46	US 4749430 A	U	19880607		Method
47	JP 63169709 A	J	19880713		PERMANE
48	DE 3800889 C	D	19880720		Primer
49	US 4764632 A	U	19880816		Multifu
50	US 4764403 A	U	19880816		Multila
51	US 4766160 A	U	19880823		Photo-h

US-PAT-NO: 3556305

DOCUMENT-IDENTIFIER: US 3556305 A

See image for Certificate of Correction

TITLE: COMPOSITE MEMBRANE AND PROCESS FOR MAKING SAME

----- KWIC -----

Detailed Description Text - DETX (5):

Selection of the particular adhesive, of course, must be made with particular attention not only to the nature of the surface of the adherent, but to whether or not it is adapted for deposition in a very thin layer. For this reason, adhesives which are soluble in a liquid vehicle from which they may be deposited are particularly useful. Moreover, polymeric adhesive solutes have been found to form the most versatile and suitable adhesive layer. These adhesives are often of the type which form coordinate covalent bonds, such as hydrogen bonds, with materials containing hydroxyl or carboxyl groups. Often this coordinate covalent bonding is of relatively high importance in forming a suitable bond between the adhesive and the diffusive polymer layer coated thereover than between the adhesive and the porous substrate where mechanical adhesion due to interlocking of the adhesive and substrate often allows a suitable bond. However, often van der Waals forces, covalent bonds and the like play important roles in maintaining a useful adhesive bond.

EAST Browser - L2: (487) covalent wit... [US 4003312 A] Tag: S Doc: 9/487 (SORTED) Format: KWIC						
File Edit View Tools Window Help						
	Document ID	KSc	Issue-De	Page	Tit	
1	US 3556305 A	U	19710119	6	COMPOST	US-PAT-NO: 4003312
2	DE 2357121 A	D	19740530	9	Aminimi	
3	DE 2461023 A	D	19750710	25	Prepoly	DOCUMENT-IDENTIFIER: US 4003312 A
4	US 3895166 A	U	19750715	5	Bonded	
5	US 3897585 A	U	19750729	5	Integra	TITLE: Preparing waterless lithographic printing masters by ink jet printing
6	US 3931084 A	U	19760106	10	Fluoroc	
7	US 3979538 A	U	19760907	4	Flocked	
8	US 3997349 A	U	19761214	8	Light-s	
9	US 4003312 A	U	19770118	6	Prepara	----- KWIC -----
10	US 4060081 A	U	19771129	16	Multila	
11	GB 1518371 A	D	19780719		Laminat	
12	US 4180442 A	U	19791225	10	Electro	Brief Summary Text - BSTX (4):
13	US 4243771 A	U	19810106	4	Nitrile	Briefly, the invention comprises forming an image with an ink jet printing
14	JP 57058617 A	J	19820408		MEDICAL	apparatus which comprises discharging the imaging fluid from as droplets and
15	US 4337111 A	U	19820629	4	Method	depositing it on an imaging surface in response to electrical signals which
16	US 4337111 A	D	19820629		Introdu	comprise an information pattern. In this manner, the droplets are selectively
17	US 4355078 A	U	19821019	3	Nitrile	emitted or deflected in accordance with an information source. In one
18	US 4405427 A	U	19830920	11	Electro	embodiment an uncured silicone curable to an ink releasable condition is
19	JP 58185515 A	J	19831029		TAPE DE	deposited on an ink accepting master substrate and the silicone cured to an ink
20	JP 58185515 A	D	19831029		Tape-fc	releasable condition. By varying the polarity of the incoming video signal,
21	US 4442142 A	U	19840410	3	Nitrile	the imaging material can be deposited to form an image either positive or
22	JP 59098183 A	D	19840606		Joining	negative in sense. In a second embodiment, a catalyst is deposited in image
23	US 4460759 A	U	19840717	7	Adhesiv	configuration on an uncured silicone, the silicone cured in image configuration
24	US 4460525 A	U	19840717	10	Method	and the uncured silicone removed in the nonimaged areas. Alternatively, a
25	JP 60068083 A	J	19850418		FORMATI	photocurable material which can combine with a cured silicone can be deposited
26	US 4518449 A	U	19850521	6	Process	in image configuration on said silicone and the plate subjected to light to
27	US 4522907 A	U	19850611	14	Method	bond the imaging material thereto. A further embodiment is to deposit a light
28	US 4529772 A	U	19850716	7	Contact	insensitive shadow fluid on a light sensitive curable silicone, expose the
29	US 4533307 A	U	19850806	9	Apparat	plate to blanket illumination to cure the background nonimaged areas and remove
30	US 4536425 A	U	19850820	5	Method	the uncured silicone beneath the light insensitive shadow fluid. In addition,
31	US 4554301 A	U	19851119	9	Modifie	an ink-accepting imaging polymer or prepolymer can be applied to an adhesive
32	US 4554195 A	U	19851119	6	Ceramic	elastomer such as a silicone, which has sites for the covalent attachment of
33	US 4572828 A	U	19860225	4	Method	the imaging material, and the materials chemically bonded to one another.
34	US 4588838 A	U	19860513	9	Diurea	
35	US 4588838 A	D	19860513		Addn. p	
36	US 4618688 A	U	19861021	5	Silane	
37	US 4619867 A	U	19861028		Az lacto	
38	US 4626310 A	U	19861202		Surqica	
39	EP 205145 A	D	19861217		Reactiv	
40	US 4644032 A	D	19870217		Non-qhc	
41	US 4645846 A	U	19870224		Silane	
42	US 4671740 A	U	19870609		Ceramic	
43	US 4677695 A	U	19870707		Web wit	
44	US 4692557 A	U	19870908		Encapsu	
45	US 4699843 A	U	19871013		Az lacto	
46	US 4749430 A	U	19880607		Method	
47	JP 63169709 A	J	19880713		PERMANE	
48	DE 3800889 C	D	19880720		Primer	
49	US 4764632 A	U	19880816		Multifu	
50	US 4764403 A	U	19880816		Multila	
51	US 4766160 A	U	19880823		Photo-h	

	Document ID	K	Seq	Issue	Da	Page	Title
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6	US 3931084 A	U	19760106	10	Fluoroc		
7	US 3979538 A	U	19760907	4	Flocked		
8	US 3997349 A	U	19761214	8	Light-s		
9	US 4003312 A	U	19770118	6	Prepari		
10	US 4060081 A	U	19771129	16	Multila		
11	GB 1518371 A	D	19780719	13	Laminat		
12	US 4180442 A	U	19791225	10	Electro		
13	US 4243771 A	U	19810106	4	Nitrile		
14	JP 57058617 A	J	19820408	6	MEDICAL		
15	US 4337111 A	U	19820629	4	Method		
16	US 4337111 A	D	19820629	9	Introdu		
17	US 4355078 A	U	19821019	3	Nitrile		
18	US 4405427 A	U	19830920	11	Electro		
19	JP 58185515 A	J	19831029		TAPE DP		
20	JP 58185515 A	D	19831029		Tape-fc		
21	US 4442142 A	U	19840410	3	Nitrile		
22	JP 59098183 A	D	19840606		Joining		
23	US 4460759 A	U	19840717	7	Adhesiv		
24	US 4460525 A	U	19840717	10	Method		
25	JP 60068083 A	J	19850418		FORMATI		
26	US 4518449 A	U	19850521	6	Process		
27	US 4522907 A	U	19850611	14	Method		
28	US 4529772 A	U	19850716	7	Contact		
29	US 4533307 A	U	19850806	9	Apparat		
30	US 4536425 A	U	19850820	5	Method		
31	US 4554301 A	U	19851119	9	Modifie		
32	US 4554195 A	U	19851119	6	Ceramic		
33	US 4572828 A	U	19860225	4	Method		
34	US 4588838 A	U	19860513	9	Diurea		
35	US 4588838 A	D	19860513		Addn. p		
36	US 4618688 A	U	19861021	5	Silane		
37	US 4619867 A	U	19861028		Azlacto		
38	US 4626310 A	U	19861202		Surgica		
39	EP 205145 A	D	19861217		Reactiv		
40	US 4644032 A	D	19870217		Non-qhc		
41	US 4645846 A	U	19870224		Silane		
42	US 4671740 A	U	19870609		Ceramic		
43	US 4677695 A	U	19870707		Web wit		
44	US 4692557 A	U	19870908		Encapsu		
45	US 4699843 A	U	19871013		Azlacto		
46	US 4749430 A	U	19880607		Method		
47	JP 63169709 A	J	19880713		PERMANE		
48	DE 3800889 C	D	19880720		Primer		
49	US 4764632 A	U	19880816		Multifu		
50	US 4764403 A	U	19880816		Multila		
51	US 4766160 A	U	19880823		Photo-h		

US-PAT-NO: 4337111

DOCUMENT-IDENTIFIER: US 4337111 A

TITLE: Method of obtaining strong and durable adhesion to rubber through chemical covalent bonds

----- KWIC -----

Brief Summary Text - BSTX (6):

Concentrated acid etching, oxidation, and radiation treatments particularly in the presence of oxygen also can provide the possibility for covalent bond formation with adhesive but these drastic treatments also break covalent bonds near the rubber surface resulting in stressed and often brittle layers.

Brief Summary Text - BSTX (11):

The strength of attachment between the coating polymer and the rubber, and between the coating polymer and the adhesive depends on the number of covalent bonds formed. The number of covalent bonds formed is, in turn, dependent on the establishment of intimate interaction between the coating polymer and the rubber and between the coating polymer and the adhesive and on the number, the type and the reactivity of chemical functional groups present in each of these materials.

Detailed Description Text - DETX (17):

The feature of the method that produces the advantages is the utilization of the vulcanization process to introduce covalent chemical bonds between the vulcanized rubber and the adhesive system.

Claims Text - CLTX (1):

1. A method for introducing covalent bonds between vulcanized rubber and an adhesive comprising the steps of:

	Document ID	KS	Issue	Da	Page	Tit
1	US 6468660 B2	U	20021022	14		Biocomp
2	US 6428579 B1	U	20020806	24		Implant
3	US 20020103538	U	20020801	13		Biomate
4	US 6410044 B1	U	20020625	14		Crossli
5	US 20020007217	U	20020117	13		Surface
6	US 6183516 B1	U	20010206	5		Method
7	US 5997517 A	U	19991207	8		Bonding
8	US 5782908 A	U	19980721	6		Biocomp
9	US 5607475 A	U	19970304	6		Biocomp
10	US 5354329 A	U	19941011	12		Vascula
11	US 4769030 A	U	19880906	7		Monomer
12	US 4060081 A	U	19771129	16		Multila

US-PAT-NO: 6468660

DOCUMENT-IDENTIFIER: US 6468660 B2

TITLE: Biocompatible adhesives

----- KWIC -----

Detailed Description Text - DETX (7):

The epoxyamine in the adhesive has unreacted epoxy groups that can react to form chemical bonds with a variety of functional groups including, for example, thiols, alcohols, amines and the like. The substrates may include inherently or a modified to include the functional groups that are reactive with the epoxyamine. Chemical bonding as referred to herein refers to all types of chemical bonding, including covalent bonding. In preferred embodiments, the epoxyamine in the adhesive forms covalent bonds with the substrates.

Detailed Description Text - DETX (51):

Application of the adhesive as a coating over the selected portion of the substrate is generally sufficient to provide strong association. The strong association of the adhesive coating can be due to natural attractions between the substrate material and the adhesive, covalent bonding with the substrate, natural wetting effects of the adhesive on a surface and/or other similar effects.

Current US Cross Reference Classification - CCXR (5):

623/2

	Document	ID	KS	Issue	Da	Page	Tit
1	US	6468660	B2	U	20021022	14	Biocomp
2	US	6428579	B1	U	20020806	24	Implant
3	US	20020103538		U	20020801	13	Biomate
4	US	6410044	B1	U	20020625	14	Crossli
5	US	20020007217		U	20020117	13	Surface
6	US	6183516	B1	U	20010206	5	Method
7	US	5997517	A	U	19991207	8	Bonding
8	US	5782908	A	U	19980721	6	Biocomp
9	US	5607475	A	U	19970304	6	Biocomp
10	US	5354329	A	U	19941011	12	Vascula
11	US	4769030	A	U	19980908	7	Monomer
12	US	4060081	A	U	19771129	16	Multila

US-PAT-NO: 4769030

DOCUMENT-IDENTIFIER: US 4769030 A

See image for Certificate of Correction

TITLE: Monomer and use thereof in crack prevention of implanted prostheses

----- KWIC -----

Detailed Description Text - DETX (8):

When the monomers according to this invention are bonded to a substrate, the bond is covalent in nature, typically by virtue of an allophanate type of bonding, rather than being an interpenetrating type of bonding, in order to provide especially advantageous hydrolytic stability and strength when compared with other adhesives.

Current US Original Classification - CCOR (1):

623/1.49

EAST Browser - L2: (3) cyanoacrylat... | US 6464999 B1 | Tag: S | Doc: 1/3 (SORTED) | Format: KWIC

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	Document ID	KSc	Issue-Dr	Pag
1	US 6464999 B1	U	20021015 57	Bin
2	US 6299787 B1	U	20011009 7	Sur
3	US 6299596 B1	U	20011009 12	Met

US-PAT-NO: 6464999

DOCUMENT-IDENTIFIER: US 6464999 B1

TITLE: Bioadhesive medical devices

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Detailed Description Text - DETX (119):

The prior art teaches two types of adhesives to attach a substrate to tissues. The first type of adhesive forms permanent (covalent) bonds to tissue surfaces. For example, liquid adhesives containing monomers, oligomers, or short chain polymers may be spread on a tissue surface, and then cured with ultraviolet light, moisture, or heat to form adhesive bonds to the tissue. Because the monomers/oligomers are diffused into the surface of the tissue, they cure with the tissue layer, forming permanent covalent bonds to the tissue. A substrate adhered to a tissue surface by a covalent bonding adhesive may not be removed without tearing or breaking the substrate or the tissue surface. An example of a covalent bonding adhesive is cyanoacrylate, which is often used as a surgical glue.

United States Patent

[11] 3,556,305

[72] Inventor Jacob Shorr
Brighton, Mass.
[21] Appl. No. 717,039
[22] Filed Mar. 28, 1968
[45] Patented Jan. 19, 1971
[73] Assignee Amicon Corporation
Lexington, Mass.
a corporation of Massachusetts

[54] COMPOSITE MEMBRANE AND PROCESS FOR
MAKING SAME
7 Claims, No Drawings

[52] U.S. Cl. 210/490,
117/73, 117/76, 117/98, 117/83, 117/86, 210/500,
264/41, 264/49
[51] Int. Cl. B44d 1/14,
B01d 39/00
[50] Field of Search 210/321,
500, 490, 22, 23; 264/41, 49; 117/76F, 98

[56] References Cited

UNITED STATES PATENTS

2,960,462	11/1960	Lee et al.	210/321X
3,022,187	2/1962	Eyraud et al.	117/16
3,331,772	7/1967	Brownscombe et al.	210/23
3,417,870	12/1968	Bray	210/321
3,462,362	8/1969	Kollsman	210/321X

OTHER REFERENCES

Monsanto. Investigation and preparation of polymer films to improve the separation of water and salts in saline water conversion. U.S. Dept. of Interior, Office of Saline Water. R & D Progress Report No. 69, Dec. 1962, PP. 41—42.

Merten et al. Research and Development on Reverse Osmosis Membrane Modules. U.S. Dept. of Interior, Office of Saline Water, R & D Progress Report No. 165, Jan. 1966, pp. 1—3.

Francis et al. Second Report on Fabrication and Evaluation of New Ultrathin Reverse Osmosis Membranes. U.S. Dept. of Interior, Office of Saline Water, R & D Progress Report No. 247, April 1947, pp. 46—47.

Primary Examiner—Willaim D. Martin

Assistant Examiner—Ralph Husack

Attorney—R. W. Furlong

ABSTRACT: A novel membrane suitable for use in reverse osmosis and related separation processes, said membrane comprising (a) an anisotropic membrane comprising a thin microporous barrier skin and a thicker macroporous support layer, (b) a very thin layer of a film forming adhesive polymer over the barrier skin of hydraulically porous substrate and (c) a very thin diffusive type membrane film overlying said adhesive polymer and bound to said porous substrate by said adhesive polymer.

COMPOSITE MEMBRANE AND PROCESS FOR MAKING SAME

BACKGROUND OF THE INVENTION

For some time, investigators active in the membrane art have attempted to solve the problem of forming reasonably strong membranes obtaining maximum diffusion activated separation by forming bifunctional membranes usually of an ultrathin diffusion barrier supported on a thicker, and more rugged, substrate which provides less resistance to flow than does the diffusion barrier. Among such attempts are those disclosed in U.S. Pat. No. 2,960,462 to Lee et al., wherein a very thin film of polymer is coated on a slightly more permeable polymer to form a diffusion membrane; in U.S. Pat. No. 3,022,187 to Eyraud et al., wherein a metallic oxide film at or near one surface of a metallic substrate forms a relatively tight barrier; in U.S. Pat. No. 3,335,545 wherein Robb et al. disclose use of a thin liquid film over a porous substrate to obtain gas separation; and in U.S. Pat. No. 3,225,107 wherein Kirland et al. disclose grafting a thin polymeric coating on at least one side of a polymeric membrane. Moreover, a considerable amount of work has been done on so-called "dynamically formed" membranes, i.e., membranes formed by taking a relatively porous substrate and continuously coating the substrate with a polymeric film material which is maintained in dilute solution in the liquid mass being subject to separation. This continuous deposition is required because the polymeric film is subject to being carried into the pores and through the porous substrate. Moreover, the films which are sufficiently soluble in the liquid mass being separated are usually subject to lateral erosion in continuous process devices. The problems associated with the formation of "dynamically formed" membranes are indicative of the problems generally encountered by those trying to form an ultrathin diffusive polymer on a hydraulically porous substrate.

By hydraulically porous substrate is meant one whose minimum average pore size is about 10 angstroms, thus making it permeable to fluid flow without regard to material of construction. The term is meant to exclude substrates which are substantially pore free and which permit the selective passage of molecules largely by activated diffusion and like processes.

Therefore, it is an object of the instant invention to provide an improved membrane comprising a thin diffusion layer on hydraulically porous substrate.

It is a further object of the invention to provide an improved membrane for reverse osmosis separations having a surprisingly advantageous ratio of liquid flux to solute retentivity.

Another object of the invention is to provide a novel process for binding a diffusion membrane layer to a hydraulically porous substrate.

It is a further object of the invention to provide an improved method for forming a membrane dynamically.

Other objects of the invention will be obvious to those skilled in the art on their reading of the instant application.

SUMMARY OF THE INVENTION

The present invention has achieved these objects by forming a novel tripartite membrane comprising a selected anisotropic porous substrate, an ultrathin adhesive layer over the porous substrate, and a thin diffusive membrane formed over the adhesive layer and bound to the substrate by the adhesive layer.

The adhesive polymer is conveniently coated on the substrate by dipping the selected porous substrate into a dilute solution of the adhesive polymer or otherwise forming a thin coat under low-pressure conditions whereby the adhesive polymer is largely retained on the substrate surface, not pushed into the pores thereof. For this reason, adhesive polymers which are sparingly soluble in water are most easily utilized. Since many separation processes involve the diffusion of water through a membrane, such water soluble adhesive polymers also provide in most cases the least resistance to the

desired flow properties of the finished membrane. However, when separations which do not involve the transmission of water are to be carried out, the adhesive polymer may be selected for its solubility in some other vehicle for deposition upon the porous substrate.

By adhesive layer is meant a very thin layer, not more than about 1500 angstroms, preferably less than 500 angstroms, in thickness, of a substance capable of holding materials together by surface attachment. More particularly, the adhesive must be such that (1) it is capable of acting as a holding adhesive; i.e., capable of attaching one adherent to another and holding them in place and (2) it is capable of acting as a sealing adhesive wherein it provides a joint between the two adhesives which, in effect, aids in sealing the adjacent surface of the anisotropic porous substrate adherent. Such an adhesive coat is believed to function not only as a means for bonding the diffusive membrane formed thereover to the substrate, but also is believed to form a protective coating over the substrate which prevents the diffusive membrane material from itself getting into the pores of the substrate.

Selection of the particular adhesive, of course, must be made with particular attention not only to the nature of the surface of the adherent, but to whether or not it is adapted for deposition in a very thin layer. For this reason, adhesives which are soluble in a liquid vehicle from which they may be deposited are particularly useful. Moreover, polymeric adhesive solutes have been found to form the most versatile and suitable adhesive layer. These adhesives are often of the type which form coordinate covalent bonds, such as hydrogen bonds, with materials containing hydroxyl or carboxyl groups. Often this coordinate covalent bonding is of relatively high importance in forming a suitable bond between the adhesive and the diffusive polymer layer coated thereover than between the adhesive and the porous substrate where mechanical adhesion due to interlocking of the adhesive and substrate often allows a suitable bond. However, often van der Waals forces, covalent bonds and the like play important roles in maintaining a useful adhesive bond.

It is generally preferred to have each of the substrate, adhesive, and diffusive polymer formed of organic polymeric material each of which material does not have a secondary transition temperature in the temperature range in which the membrane is intended to be used in separation processes. This is to minimize the possibility that differences in thermal expansion coefficients between the various layers of the composite layer will mechanically disrupt any of the component layers.

One procedure which has been found to be particularly advantageous is to use as an adhesive layer a polymeric adhesive which has only sparing solubility in the primary liquid of the medium to be subjected to processing. This usually assures the continued adhesive quality of the adhesive layer throughout the contemplated life of the membrane.

Poly(methyl vinyl ether/maleic anhydrides) sold under the trade designation Gantrez AM by General Aniline & Film Corp. are useful adhesive polymers. Conveniently used is Gantrez AN-139 of specific viscosity of about 1 to 2. Solutions of this material are compatible with solutions of other useful adhesive polymers such as sodium polyacrylate sold under the trade designation "Acrysol" by Rohm & Haas Co.; such naturally derived products as albumin, sodium alginate, sodium carboxymethyl cellulose, starch, oxidized starch, dextrin, casein; carboxyvinyl polymers such as those sold under the trade name "934" by Goodrich Chemicals, Inc.; hydroxyethyl cellulose; dimethylhydantoin formaldehyde resin; polyvinyl alcohol; methyl cellulose; the phenol formaldehyde resins sold under the trade name "Plyophen P-398" by Reichold Chemical Co.; "Polyox" WSR-35 and WSR-70 sold by Union Carbide Corp. which are poly(ethylene oxide); poly(vinyl methyl ether), polyvinyl pyrrolidone; vinylpyrrolidone/vinyl acetate copolymer; polyacrylamide such as sold by Dow Chemical Co. under the trade designation "Separon NP-20"; the styrene/maleic anhydride copolymer sold under the trade designation Stymer S by Monsanto Chemical Co.; and the like.

The synthetic and natural polymers in the aforesaid list are typical of adhesive polymers which may be utilized in the practice of the invention. The precise selection of an adhesive polymer will be made with reference to the chemical nature of the porous substrate and the material from which the overlying diffusion polymer is to be prepared. Coatings of the adhesive polymer are normally not more than about a molecular layer or two thick, i.e., as thin as possible but sufficiently thick to provide an effective boundary layer between the porous support and the diffusion membrane to be deposited over the adhesive area.

The diffusion-type membrane film which is adhesively bonded to the anisotropic porous substrate by an adhesive polymer may be formed of any of the organic or inorganic, polymer or gellike, film forming materials known to the art. For example, most of the polymers which have been used in the forming of "dynamically formed" membranes can be used. In the process according to the instant invention and in articles formed thereby such polymers and gellike materials need not be constantly replaced because they are not at all swept through a porous substrate. Moreover, because of the adhesive polymer layer over the anisotropic porous substrate, a very thin film of the polymer or gel can be fixed at the surface and it is not subject to severe erosion by process fluid as would be the case were there no bond with the adhesive layer. Utilizing this aspect of the invention with aqueous systems, it is most advantageous that the adhesive layer be more soluble than the diffusive-type membrane film mounted thereover. In this way the advantage of an adhesive capable of promoting optimum diffusive flow of water can be achieved without exposing the membrane to the highly mobile liquid moving in the cell in which the membrane is mounted. The composite thickness of adhesive and overlying membrane is less than 2 microns and most advantageously less than 2,000 angstroms.

Such materials as the hydrous oxides of trivalent aluminum and iron, tetravalent silicon, zirconium, and thorium, and hexavalent uranium and other finely ground solids capable of forming gellike substances, for example clays such as bentonite and humic acid can be used. Polyelectrolytes, such as the polyanion, poly (styrene sulfonic acid), and the polycation poly (vinylbenzyltrimethyl ammonium chloride) can be used. Also found to be useful are cellulose acetate, hydrogen phthalate, cellulose acetate N,N-diethylaminoacetate, poly (4-vinyl pyridine), poly (4-vinyl pyridinium butyl) chloride and poly (vinyl pyrrolidone). There can also be used polyvinyl alcohol or a mixture of polyvinyl methyl ether with a copolymer of vinyl methyl ether with maleic anhydride. These materials are most advantageously coated on the adhesive polymer layer by "dynamically forming" the coating over the adhesive layer. This procedure wherein the material is dissolved in a dilute solution which is "filtered" through the membrane while the solute becomes attached to the adhesive layer, has been demonstrated to give superior distribution of the solute on the adhesive layer and, consequently, a superior membrane.

Thus, membranes formed according to the instant invention have a number of significant advantages over dynamically formed membranes of the prior art. First the nonerosive qualities thereof allow them to be used in processing a wide variety of solutions with no requirement that membrane forming polymer "makeup" be included in the solution. Secondly, they have operating characteristics relatively independent of concentration. This differs markedly from most dynamically formed membranes wherein the interstices of the porous substrate become coated with the membrane forming polymer, with the result that a Donnan exclusion-type action takes place, thereby making the separation efficiency dependent on maintaining a suitably low solute concentration in the feed.

Surprisingly, it has also been discovered that membranes of the instant invention wear and perform best in the thin channel systems known to the art which provide high velocity non-turbulent flow.

It is desirable to distinguish one basic membrane-type filter from the anisotropic porous membrane supports useful in the

invention. This is the membrane of isotropic, sometimes called homogeneous, structure whose flow and retention properties are independent of flow direction. Such structures are typically produced in the form of sheets of from 0.1 to 0.010 inch in thickness. Most such membranes are analogous to conventional filters and are virtually nonretentive for solutes of molecular weight under about 1 million. A few such membranes are capable of retaining some larger protein molecules. When attempts are made to prepare such membranes having a capability of retaining much smaller molecules, large decreases in hydraulic permeability often occur. Such decreases result in too-low solvent flow rates through the membrane or restrict the usage of these isotropic membranes to a relatively few practical applications. Moreover, such isotropic membranes are susceptible to relatively easy plugging by trapped solutes. In some membranes of this type, usually those which have relatively small pore sizes, some small degree of anisotropy is achievable, but such membranes do not function properly when utilized in this invention.

The porous substrate should be a highly anisotropic and porous membrane of the type described in the commonly owned and copending patent applications, Ser. No. 669,648 filed Sept. 21, 1967 by Alan S. Michaels, now abandoned, and Ser. No. 545,298 filed on April 26, 1966 by Peter N. Rigopoulos, the latter now abandoned and replaced by Ser. No. 850,263 filed Aug. 14, 1969. The former application is entitled High Flow Membranes; the latter application is entitled Permeable Membrane and Method of Making and Using Same. Such membranes are advantageous because they combine, in an integral substrate member (1) a barrier skin on one side thereof which has sufficiently small micropores to form a highly desirable "surface" on which to form—and retain—the adhesive polymer film and (2) a macroporous substructure which offers no significant additional resistance to liquids which pass the aforesaid barrier layer, but does provide mechanical support for the integral barrier layer and subsequently coated polymer layers superimposed upon it.

The anisotropic porous substrates which are most advantageously utilized have distinctive barrier skins of from about 0.1 to 5 microns in thickness. The average pore size is in the millimicron range, i.e. from 10 angstroms to 1,000 angstroms. Surfaces having pore sizes in this range provide the most suitable method of maintaining the membranes operating characteristics for prolonged periods of operation. These highly anisotropic membranes are to be carefully distinguished over some membranes presently on the market which are alleged to possess some degree of anisotropy, but which are in fact far more closely related in pore size, gradient of pore size from one face of the membrane to the other, and operating characteristics to the isotropic membranes described above. One such membrane which may have a slight anisotropic character is that sold under the trade designation MF-Millipore.

These anisotropic porous substrates useful in the present invention are highly anisotropic, submicroscopically porous, membranes formed of polymers having good mechanical integrity, most advantageously those crystalline and/or glassy thermoplastic polymers known to the art. These supports are described in the commonly owned and copending U.S. Pat. application, Ser. No. 669,648. By crystalline and glassy polymers are meant those materials which possess from about 5 to 50 percent by weight crystallinity as measured by X-ray diffraction techniques known to the art and/or a glass transition temperature (T_g) of at least about 20° C. Particularly advantageous are polymers of inherently low water sorptivity, which unlike the cellulose acetate materials known to the membrane art may be allowed to dry during storage without losing their beneficial mechanical and processing characteristics. These polymers are those having water absorptivities of less than about 10 percent by weight of moisture at 25° C., and 100 percent relative humidity.

Such anisotropic membranes are prepared by:

1. forming a casting dope of a polymer in an organic solvent;
2. casting a film of said casting dope;

3. preferentially contacting one side of said film with a diluent characterized by a high degree of miscibility with said organic solvent and a sufficiently low degree of compatibility with said casting dope to effect rapid precipitation of said polymer; and
4. maintaining said diluent in contact with said membrane until substantially all said solvent has been replaced with said diluent.

The submicroscopically porous anisotropic membranes described in the copending application consist of a macroscopically thick film of porous polymer, usually more than about 0.002 and less than about 0.050 of an inch in thickness. One surface of this film is an exceedingly thin, but relatively dense barrier layer or "skin" of from about 0.1 to 5 microns thickness of microporous polymer in which the average pore diameter is in the millimicron range, for example from 1 to 1,000 millicrons—i.e., about one-tenth to one-hundredth the thickness of the skin. The balance of the film structure is a support layer comprised of a much more coarsely porous polymer structure through which fluid can pass with little hydraulic resistance. When such a membrane is employed as a "molecular filter" with the "skin side" in contact with fluid under pressure, virtually all resistance to fluid flow through the membrane is encountered in the "skin," and molecules or particles of dimensions larger than the pores in the "skin," and molecules or particles of dimensions larger than the pores in the "skin" are selectively retained. Because the skin layer is of such extraordinary thinness, the overall hydraulic resistance to fluid flow through the membrane is very low; that is, the membrane displays surprisingly high permeability to fluids.

Some such membranes are obtainable from Amicon Corp. under the trade designation Diaflo XM-50. The procedure used in forming the porous substrate used in the illustrative working example follows:

30 grams of a polysulfone polymer sold by 3M Co. under the trade designation Polymer 360, was dissolved at about 50° or 60° C. in 100 cc. of dimethylsulfoxide (DMSO). The resultant solution was cooled to about 25° C. and centrifuged down to remove any sedimentary matter therefrom. Next, the solution was drawn down into a film 12 mils thick. This casting was done on a clean glass surface with the edges of the casting overlying a taped perimeter which is to provide means to assist in removing the casting from the glass without tearing it.

The casting was allowed to level for 1 minute and then submerged into a gently circulating water bath for a period of about 20 minutes. This water bath is maintained at about 25° C. Next, the resulting membrane was stripped off the glass plate and cut into the desired membrane shape.

The membrane so formed was found to reject completely a polysaccharide of about 100,000 average molecular weight, to reject about 75 percent of a polysaccharide having about a 20,000 molecular weight. These rejections were measured with 1 percent aqueous solutions under 50 p.s.i.g. operating pressure and at about 30° C. At 100 p.s.i.g. applied pressure and 25° C. the membrane exhibited a flux of about 50 gallons per square foot per day to distilled water.

The material Polymer 360 is particularly advantageous for use because, it has been discovered, the rheological properties of this polymer allow the formation of a porous network having an unusually high hydraulic permeability and yet being highly retentive of macromolecular solutes. This polymer is a thermoplastic having a chain formed of diphenyl and phenyl groups which groups are linked by sulfone groups and oxygen atoms. The inherent viscosity of the material is 0.42 to 0.46 as measured in a 1 percent solution of the material in dimethylformamide.

The working examples which are set forth below were carried out in a so-called thin channel cell of essentially rectangular dimensions having ¾-inch entrance and exit ports at either end thereof. Exposed membrane surface was 4.75 inches by 1.5 inches. Depth of the channel was 0.010 inch. Flow through

the cell was maintained at about 100 cc. per minute or a flow velocity of 16 cm. per second.

EXAMPLE 1

An anisotropic membrane, formed of Polymer 360 as described above, was soaked for 4 hours in an aqueous solution containing 1,000 parts per million of poly(vinyl methyl ether) of the type sold under the trade designation Gantrez M-155 by General Aniline & Film Corp. The membrane was then mounted in a stainless steel membrane separation cell with the barrier skin layer facing in what may be called the upstream direction.

An aqueous solution comprising 2,000 parts per million of a poly(vinyl alcohol) sold under the trade designation Elvanol 50-42 by E. I. DuPont de Nemours & Co., Inc., was prepared. A pressure of 100 p.s.i.g. was exerted on the solution as it was "filtered" through the adhesive coated anisotropic membrane for 30 minutes. During this period a thin diffusive membrane of poly(vinyl alcohol) formed over the adhesive.

After a 30 minute period, the system was flushed and a 1 percent aqueous sugar solution was passed through the resultant membrane at 1,500 p.s.i.g. The object of this experiment was to evaluate the effect of the membrane in retaining sugar while passing water therethrough. The test was run over a period of 15 hours during which retentions of 85 percent to 92 percent sugar were achieved with an average water flux of about 50 gallons per square foot per day.

EXAMPLE 2

An anisotropic membrane of the type described in Example 1 was soaked for 2 hours in a solution containing 1,000 parts per million poly(vinyl methyl ether) sold under the trade designation Gantrez 155 by General Aniline & Film Corp.

The membrane was mounted as before and an aqueous polymer solution comprising 1,000 parts per million of poly(methyl vinyl ether/maleic anhydride) sold under the trade designation Gantrez AN-139 by General Aniline and Film Corp. and 200 parts per million of the aforesaid poly(vinyl methyl ether) was passed therethrough for 30 minutes. After the system was flushed with water, and a 2 percent sugar solution was passed therethrough at 1,500 p.s.i.g. About 85 percent of the sugar was retained. Flux rates were maintained at 94 gallons per square foot per day over the 15 hour test period.

EXAMPLE 3

The same membrane preparation procedure was followed as in Example 2. Instead of a sugar solution, however, a 0.5 percent salt solution was passed through the membrane. Eighty percent of the salt was retained and a flux rate of 125 gallons per square foot per day was achieved.

I claim:

1. A membrane suitable for use in ultrafiltration, reverse osmosis, and other such separation processes, said membrane comprising:

1. a porous substrate formed of a highly anisotropic polymeric membrane having a. a barrier layer at one surface thereof comprising micropores from 15 to 1,000 angstroms in diameter and having a thickness from about 0.1 to 5 microns and b. a macroporous support layer;
2. an adhesive polymeric layer having a maximum thickness of about 1,500 angstroms coated on said substrate; and
3. a diffusive polymer or gel-like film bonded to said barrier layer of said porous substrate by said adhesive layer.

2. A membrane as defined in claim 1 wherein the maximum thickness of said adhesive polymeric layer is about 500 angstroms.

3. A membrane as defined in claim 1 wherein said adhesive layer consists of an alkyl vinyl ether polymer or copolymer.

4. A membrane as defined in claim 1 wherein said diffusive film is polyvinyl alcohol or a mixture of polyvinyl methyl ether with a copolymer of methyl vinyl ether with maleic anhydride.

5. A membrane as defined in claim 1 wherein the composite thickness of said adhesive layer and a diffusive film overlying said layer is less than about 2 microns.

6. A membrane as defined in claim 1 wherein said porous substrate is formed of a polysulfone polymer.

7. A process for making a membrane suitable for use in ultrafiltration, reverse osmosis, and other such separation processes which comprises providing a porous substrate formed of a highly anisotropic polymeric membrane having *a*. a barrier layer at one surface thereof comprising micropores

from 15 to 1,000 angstroms in diameter and having a thickness from about 0.1 to 5 microns and *b*. a macroporous support layer, coating said substrate with a solution of an adhesive polymer to thereby deposit on the surface of the substrate an adhesive polymeric layer having a maximum thickness of about 1,500 angstroms, and filtering through said substrate from the surface having the barrier layer a dilute solution of polymer or gellike material to form a diffusive film bonded to said adhesive layer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,556,305 Dated January 19, 1971

Inventor(s) Jacob Shorr

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 20, "Kirland" should read -- Kirkland --.
Column 2, line 65, after "trade name" insert -- Carbopol -
Column 5, line 17, "millicrons" should read -- millimicron
line 54, "polysaccharide" is misspelled; Column 6, line 66
"gellike" should read -- gel-like --. Column 8, line 8,
"gellike" should read -- gel-like --.

Signed and sealed this 4th day of May 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, J
Commissioner of Patent